



*# AF/IFW/1746*  
**PATENT**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

IN RE APPLICATION OF: Eric J. BERGMAN  
APPLICATION NO.: 09/811,925  
FILED: MARCH 19, 2001  
FOR: **METHODS FOR CLEANING SEMICONDUCTOR  
SURFACES**

EXAMINER: Z. EL-ARINI  
ART UNIT: 1746  
CONF. NO: 1111

**TRANSMITTAL LETTER**

Mail Stop Appeal Brief - Patents  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

Further to the Notice of Appeal submitted April 29, 2004, enclosed herewith is Applicant's Appeal Brief Under 37 CFR § 1.192, in triplicate; a check for the filing fee in the amount of \$330; and a return postcard.

Dated: May 14, 2004

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Debbie Gilbert  
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**APPEAL BRIEF UNDER 37 CFR § 1.192**

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Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

This Appeal Brief is in response to the Final Office Action mailed February 4, 2004. A Notice of Appeal was filed on April 29, 2004. The pending claims are attached as an Appendix.

[Continued on the next page.]

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**Appeal Brief Under 37 CFR § 1.192(c)**

1. Real party in interest – Semitool, Inc.
2. Related appeals and interferences – None
3. Status of claims – Claims 98-100, 102-106, and 119-130 stand rejected;  
Claims 1-97, 101, and 107-118 have been cancelled;  
Claims 98-100, 102-106, and 119-130 are appealed.
4. Status of amendments – No amendments have been filed subsequent to the February 24, 2004 Final Office Action.
5. Summary of Invention – The appealed claims describe methods for cleaning a semiconductor wafer. A heated aqueous solution is sprayed onto the wafer. Ozone gas is provided around the wafer, moves through the solution, and contacts the contaminants or organic materials (such as photoresist) on the surface of the article. The contaminants are oxidized and carried away by the solution. See pages 11-17 of the application.
6. Issue – There is only one issue on appeal: Whether claims 98-100, 102-106, and 119-130 are patentable under 35 U.S.C. §103 over Ohmi et al. (U.S. Patent No. 5, 487,398) in combination with JP H04-125927 (“JP’927”).
7. Grouping of Claims – Claims 98-100, 102-106, and 119-121 are in Group I. The remaining appealed claims 122-130 are in Group II. The claims in Group I are separately patentable for the reasons set forth below in the Argument.

8. Argument

A. The Appealed Claims

Three independent claims are appealed: Claim 98 in Group I and Claims 122 and 127 in Group II. Claim 98 describes rotating a wafer; spraying the wafer with a heated aqueous solution to form a thin aqueous film thereon; simultaneously providing ozone gas into the chamber; and oxidizing the contaminants on the wafer. Claims 122 and 127 in Group II describe spraying the wafer or article with a heated aqueous solution while simultaneously contacting the surface of the wafer with ozone to oxidize contaminants on the wafer surface.

B. The Ohmi et al. Reference

1. No Use of Ozone.

Turning first to the claimed ozone element and the Ohmi et al. patent, Claim 98 describes "providing ozone gas into the processing chamber in an amount sufficient to create an oxidizing effect on the surface of the wafer to oxidize contaminants thereon;" In contrast, Ohmi et al. uses water having dissolved ozone, but strives to keep ozone out of the chamber. Here is what Ohmi et al. says about ozone:

"For the present invention, it is preferable to continuously flow an inert gas in the way of downflow. By using the atmosphere of an inert gas, it is possible to prevent an object to be cleaned from being exposed to the air and an oxide film from being formed." Col. 5, lines 42-44.

"From this point of view, it is preferable to keep the oxygen content in an inert gas at 100ppb or less, more preferable to keep int at 100 ppb or less, and most preferable to keep it at 1 ppb or less". Col. 5, lines 57-60.

Ozone is of course made from oxygen, and necessarily includes oxygen. Even highly pure ozone quickly comes to include significant oxygen, because ozone is reactive and unstable, and easily breaks back down to oxygen. ( $O_3$  becomes  $O_2$ ). The description in Ohmi et al. of use of an inert atmosphere teaches away from the providing of ozone step in claim 98.

In Ohmi et al., ozone is dissolved into water. (Col. 6, lines 40-41; Col. 10, lines 34-36). The ozone stays in the liquid and is removed as waste with the used liquid. (Col. 12, lines 63-67). In Ohmi et al., ozone is not provided as a gas into the chamber, as in claims 98 and 104, 105, 106 and 119.

2. No Use of a Heated Solution.

Consistent with this dissolved ozone method, there is no heating step or use of a heated liquid in Ohmi et al. Indeed, temperatures or heating are simply not mentioned at all anywhere in Ohmi et al. Hence the heated liquid element in each of the appealed claims is not suggested in Ohmi et al.

3. No Spraying.

Ohmi et al. also teaches away from the claimed spraying step. Ohmi et al. teaches a method of feeding ozone-added ultrapure water to the surface of a workpiece to oxidize organic contaminants on the workpiece surface (col. 14, lines 29-31). Feeding here is not spraying. Here is what Ohmi et al. says about feeding versus spraying:

"Though the cause is unknown, the inventor of the present invention attempted dropping feed of feeding [sic] every several drops of a chemical solution onto the surface instead of spraying the chemical solution onto the surface. As a result, it was found that the number of contamination sources in the case of dropping feed [sic] was less than the number of contamination sources in the case of spraying" (col. 4, lines 13-19, emphasis added). This statement teaches away from spraying because it contends that spraying results in more contamination than drop feeding.

"Therefore, as the result of repeating the experiment, it was found that it was very important to continuously feed a chemical solution or ultrapure water not in the form of a drop but in the form of a fluid. That is, it is important to feed a chemical solution not intermittently but continuously like city water coming out of a faucet." (Col. 4, lines 21-24, emphasis added).

This statement teaches away from spraying. Spraying is a stream of drops. Here, Ohmi states that it is important not to use drops.

"In the case of spraying, it is estimated that a chemical solution does not uniformly cover an object to be cleaned because it is fed in the form of a fog and therefore cleaning at a high cleanliness cannot be achieved (Col. 4, lines 60-63)."

This statement teaches away from spraying.

"Moreover, it is preferable to arrange the cross section of the solution exit so that it is horizontal to an object to be cleaned. When using the above nozzle, it is possible to uniformly clean the surface of the object by dropping a chemical solution or ultrapure water just under the solution exit as a continuous fluid so that a dropping point comes to the rotational center of the object because the dropped chemical solution or ultrapure water is uniformly expanded in the surface due to a centrifugal force." (Col. 10, lines 1-8).

This statement, describing "dropping" a solution or water as a "continuous" fluid, teaches away from spraying.

Thus, Ohmi et al. teaches away from using a spraying method, and teaches using a feeding method instead of spraying.

The February 4, 2004 Final Office Action, in the "Response to Arguments" section, asserts that Ohmi et al., at col. 7, lines 35-38 (the "back cleaning section"), does teach spraying, because it states that "it is preferable to spray a chemical solution on both the surface and the back of an object to be cleaned." The Final Office Action further states that "feeding the cleaning solution would inherently include spraying."

Taken as a whole, however, at most Ohmi et al. teaches spraying only the back or bottom of the wafer, and not the top or device side. For example, col. 10, lines 19-32, of Ohmi et al. describe a back-cleaning spray nozzle that is used to clean only the back of the workpiece. Similarly, claim 1 of Ohmi et al. recites first and second nozzles

for "feeding" chemical solutions to the surface of an object, and third and fourth nozzles for "spraying" chemical solutions onto the back of the object.

Thus, Ohmi et al. distinguishes between "feeding" and "spraying," and, at a minimum, clearly teaches away from spraying the top surface. Indeed, with regard to the nozzles used to clean the top surface, Ohmi et al. emphasizes that its nozzle rack is "not the spraying type".

"Moreover, because this is not the spraying type such as an existing shower nozzle, it is possible to smoothly and continuously feed a chemical solution and ultrapure water at a constant flow rate." (col. 9, lines 53-56).

Accordingly, Ohmi et al., taken as a whole, does not reasonably suggest spraying a front side or surface of a wafer being cleaned. Thus, in addition to not suggesting use of a heated aqueous solution, and teaching away from use of ozone, Ohmi et al. also teaches away from spraying the front side of the wafer.

### C. The JP H04-125927 Reference

#### 1. No Use of Ozone on a Wet Wafer.

Turning now to the secondary reference, JP 'H04(1992)-125927 discloses a method of spraying hot sulfuric acid (which may include added water-containing ozone) onto the surface of a wafer in an ozone-containing atmosphere. As shown in Fig. 1, and as described in paragraph 55 of the translation, in JP'927, the wafers are first heated to 120°C using a heater, within a quartz tank containing ozone gas. The ozone gas, acting on the heated wafers, oxidizes organic material or contaminants on the wafer surface. Since the wafer surface is above boiling, it is clear that during this step,



the wafer surface is dry, and that this is a dry ozone ashing process. Then, when the sufficient ozone gas in the tank is consumed, hot sulfuric acid (optionally including water containing ozone) is sprayed onto the wafer surface.

In JP'927, ozone gas reacts with contaminants on the dry surface of the wafer. In all of the appealed claims, the surface of the wafer being cleaned is necessarily wet, since the wafer is sprayed with a heated aqueous solution. Claim 98 specifically describes formation of a thin aqueous film on the wafer. In JP'927, there is no thin aqueous film formed, or any film at all. The wafers are fixed in place and do not rotate, so there is no means for forming or maintaining a thin aqueous film.

D. There is No Suggestion to Combine the References

Turning now to the combination of Ohmi et al. and JP'927, which is the basis for all of the rejections, initially, the combination is improper. There is no suggestion in either reference to combine that reference with the other. Ohmi et al. uses dissolved ozone and is silent on temperature. It is well known that the solubility of ozone gas in water, like most gases, decreases with increasing temperature. The attached chart visually demonstrates this inverse relationship. This reduction in solubility of gases with increasing temperature is why many prior art ozone methods use chilled water. Matsuoka EP548596 which was applied against the claims in the 12/5/01 Office Action, expressly teaches use of ozone at room temperature, and notes that heating is disadvantageous. See also Matthews, U.S. Patent No. 5,464,480, of record, which teaches use of dissolved ozone in water chilled to 0-15°C.

JP'927 discloses use of a heated sulfuric acid solution which may include water containing ozone. Even assuming that the claimed heated aqueous solution is met by

the hot sulfuric acid solution in JP'927, there is still no motivation to combine the heated solution element of JP'927 with Ohmi et al., since adding heat to the solution in Ohmi et al. would only reduce the amount of ozone that can be dissolved in that solution. This would impede whatever the intended function of the ozone is in Ohmi et al.

Applicant agrees with the Examiner's comment at page 4 of the 10/28/03 office action that, (with the added proviso that with all other things being equal), the higher the temperature, the greater the oxidation effect from the ozone. However, here all other things are not equal. The other factor of course is the amount of ozone available to cause oxidation. If the heating aspect of JP'927 is used with Ohmi et al., the concentration of ozone dissolved in the liquid becomes negligible. So even though the temperature may be high, the oxidation rate is low, because there is little ozone dissolved in the solution, and correspondingly little ozone available to oxidize contaminants.

The basis for the rejections requires that the heating aspect and the ozone environment of JP'927 be combined with Ohmi et al. However, adding the ozone environment of JP'927 to Ohmi et al. conflicts with Ohmi et al., since Ohmi et al. strives to avoid oxidation and the oxide layers apparently caused by an ozone gas environment. This is why Ohmi et al. uses an inert gas environment.

Another reason the combination is improper is because Ohmi et al. teaches away from spraying. Hence, Ohmi et al. cannot properly be reasonably combined with a reference that teaches spraying such as JP'927 to yield the claimed methods ("It is improper to combine references where the references teach away from their

combination" MPEP §2145(X)(2)). For these reasons, the combination of Ohmi et al. with JP'927 is improper.

If the Board determines that the combination of Ohmi et al. with JP'927 is proper, then the following additional comments are relevant.

E. The Claims Are Not Obvious Over the Combination

JP'927 discloses a process temperature of 120°C. At this temperature the aqueous solution would be boiling. Consequently, it is not clear how the combination of Ohmi et al. and JP'927 could provide the thin aqueous film of claim 98, or the temperature range of claim 132.

In Ohmi et al., the use of water containing dissolved ozone is just the first step of five cleaning steps. See Fig. 1 and Col. 6, Lines 26-39; Col. 11, lines 52-53; and Col. 12, lines 50-60. After using water containing dissolved ozone, Ohmi et al. then uses hydrofluoric acid; hydrogen peroxide; and ammonium hydroxide. These are all highly reactive and toxic chemicals. They are costly to buy and use, require special handling and use precautions, require special chamber materials, and can create difficult environmental disposal issues.

JP'927 similarly uses hot sulfuric acid, which like the chemistries in Ohmi et al., is also costly, toxic, and difficult to handle, use and dispose of. In contrast, in the claimed invention, cleaning is achieved via only hot water and diffused ozone. How then can the claimed methods using ozone and water be obvious over a combination of references using ozone, water, and one or more acids or caustics? Applicant submits they cannot be obvious.

The difference is due to the fact that by having very high concentrations of ozone gas in the chamber, very large amounts of ozone diffuse through the thin aqueous film, and react with contaminants on the wafer surface. The heating provided by the hot water accelerates the chemical or oxidation reactions. Use of strong acids or caustics is avoided. While Ohmi et al. uses ozone, the ozone is dissolved and not diffused through a thin aqueous film. Since the solubility of ozone gas in water is limited, even at room temperature, with the Ohmi et al. process, only small amounts of ozone can reach and react at the wafer surface. And in JP'927, since the wafer is hot and dry when exposed to ozone gas in the chamber, the result is an ashing process where contaminants are oxidized by ozone into carbon dioxide. Neither reference, or their combination, suggests the surprising and beneficial results of using a heated aqueous solution and ozone, as claimed.

F. Group I Claims

The claims in Group I are separately patentable over and above the reasons set forth above because Claim 98 describes rotating the wafer and forming a thin aqueous film, whereas the independent claims in Group II do not include these elements. The combination of Ohmi et al. and JP'927 does not render Claim 98 obvious for the following additional reasons. Ohmi et al. suggests, if anything, a thick liquid layer ("like water coming out of a faucet", Col. 4, line 26), and avoiding ozone or oxygen gas in the chamber entirely. JP'927 exposes the wafer to ozone when the wafer is dry, i.e., with no liquid film whatsoever on the wafer. Accordingly, neither reference, or their combination suggests using a heated aqueous solution forming a thin aqueous film, together with ozone, as described in the claims of Group I.

G. Conclusion

In view of the foregoing, Applicant submits that the claims are not obvious over the combination of Ohmi et al. and JP'927. Accordingly, Applicant requests that the Board reverse all of the rejections.

Dated: May 14, 2004

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## **APPENDIX – Claims in the Appeal**

(Claims 1-97, 101, and 107-118 have previously been cancelled)

98. A method for cleaning a semiconductor wafer comprising:
- (a) rotating a wafer in a processing chamber;
  - (b) spraying a surface of the wafer with a heated aqueous solution to form a thin aqueous film thereon and simultaneously providing ozone gas into the processing chamber in an amount sufficient to create an oxidizing effect on the surface of the wafer to oxidize contaminants thereon; and
  - (c) removing oxidized contaminants from the surface thereof.
99. A method as defined in claim 98 wherein the aqueous solution is water.
100. A method as defined in claim 98 wherein the aqueous solution contains an acid.
102. A method as defined in claim 98 wherein the aqueous solution is adjusted to a temperature sufficient to effect oxidation on the surface of the wafer.
103. A method as defined in claim 98 wherein the contaminants are removed by rinsing.

104. A method as defined in claim 98 wherein the ozone is injected into the processing chamber.

105. A method as defined in claim 98 wherein the ozone is admixed with a carrier gas.

106. A method as defined in claim 105 wherein the carrier gas is selected from the group consisting of oxygen, nitrogen, air and inert gas.

119. The method of claim 98 wherein the ozone is provided as a gas around the semiconductor wafer.

120. The method of claim 98 wherein the ozone is provided in an ozone/liquid solution.

121. The method of claim 98 wherein the ozone/liquid solution is supplied separately from the heated aqueous solution.

122. A method for cleaning organic material from a surface of a workpiece comprising:

(a) spraying a heated aqueous solution onto the surface of the workpiece and simultaneously contacting the surface with ozone to effect oxidation of the organic materials on the surface of the workpiece to oxidize the contaminants; and

(b) removing oxidized contaminants from the surface.

123. The method of claim 122 wherein the aqueous solution comprises water.

124. The method of claim 122 wherein the aqueous solution comprises an acid.

125. The method of claim 122 wherein the aqueous solution forms a thin aqueous film on the surface of the workpiece.

126. The method of claim 122 wherein the organic material comprises a photoresist.

127. A method for cleaning an organic material off of a surface of a semiconductor article comprising:

placing the article into a processing chamber;

spraying the surface of the article with a heated aqueous solution, while simultaneously contacting the surface of the article with ozone in an amount sufficient to oxidize the organic material;

removing the oxidized organic material from the surface of the article; and

removing the article from the processing chamber without performing a separate rinsing step.



128. The method of claim 127 further including the step of rotating the article.

129. The method of claim 127 wherein the aqueous solution and the ozone are sprayed onto the surface of the article in solution form.

130. The method of claim 127 wherein the aqueous solution is heated to a temperature between 50° C and 90° C.